

TITLE OF THE INVENTION
MAGNETIC RECORDING MEDIUM

BACKGROUND OF THE INVENTION

5 The present invention relates to a magnetic recording medium for high-density recording containing ferromagnetic fine powder as a magnetic layer. In particular, the invention relates to a magnetic recording medium having good storage property and high durability.

10 As magnetic recording medium for the applications in audio equipment, video equipment, computer, etc., a magnetic recording medium is used, which has a magnetic layer containing ferromagnetic powder dispersed in a binder, and the magnetic layer is placed on a nonmagnetic support
15 member.

 In recent years, digital recording with less deterioration of recording quality compared with conventional analog recording has been used widely in practical application, also in the field of video tape
20 recorder for home use. In general, more signals must be recorded in digital recording than in analog recording. The recording and reproducing system and recording medium used for digital recording must provide high picture quality and high tone quality and also must be designed in
25 more compact size and must have space-saving property. In this respect, there are strong demands on high-density recording.

 To achieve high-density recording, it is necessary to

turn the recording signals to shorter wavelength and recording track must be designed narrower. For this purpose, ferromagnetic powder must be finer powder with high filling ratio and the recording medium must have
5 smoother surface. Also, writing speed and reading speed to and from the recording medium must be increased. Attempts are now being made to increase the number of revolutions of cylinder or to increase carrier speed of tape.

In the equipment or devices using the magnetic
10 recording medium, there is problem in that magnetic head is contaminated because the medium and the magnetic head slide against each other. In particular, in the device for high density recording, number of revolutions of the magnetic head is high. In a digital video tape recorder, number of
15 revolutions of the magnetic head is as high as 9,600 rpm, and this is much higher compared with 1,800 rpm of an analog video tape recorder for household use, and 5,000 rpm of a video tape recorder for business use.

With the increase of sliding speed between the
20 magnetic recording medium and the magnetic head, there are now strong demands on the development of a magnetic recording medium, which has high durability and high resistance to wear or damage and has high resistance to high speed sliding movement.

25 Not only for the tape-type magnetic recording medium, but also for disk-type magnetic recording medium, high-density magnetic recording medium is required, as typically represented by Zip (Iomega Inc.), which can be rotated at

higher speed compared with the conventional type floppy disk. Thus, a magnetic recording medium with high durability and high resistance to wear and damage is required for this purpose.

5 To solve the above problems, for the purpose of providing a magnetic recording medium, which contains ferromagnetic metal powder dispersed in a binder and which has high durability in high density recording and can perform stabilized recording and reproduction, it is
10 proposed to use a magnetic recording medium, which contains various types of lubricants in the magnetic layer. It is proposed to use various types of triester or tetraester compound as lubricant when ester is used as lubricant.

For instance, JP-88021255(B) describes the use of
15 triester or tetraester lubricant obtained from trimethylolpropane, trimethylolethane or pentaerythritol. However, these lubricants have poor storage property, and the resistance to damage of the magnetic layer is low. In particular, the properties of this lubricant are not high
20 enough for high-density recording medium such as digital recording tape.

Also, JP-59065931(A) describes a magnetic recording medium using a lubricant, which simultaneously uses triester of trimethylolpropane and other diester or
25 tetraester and monoester. However, storage property of the magnetic layer is not sufficiently high, and the magnetic layer also has poor resistance to damage or wear. Further, these products are low in durability and have poor

electromagnetic transfer characteristics.

JP-61139921 (A) describes a magnetic recording medium, which uses fatty acid ester of polyhydric alcohol and phosphoric acid ester of phenoxydiethylene glycol as
5 lubricants. But, this product has magnetic layer with low storage property and low resistance to damage. Further, the product has low durability and poor electromagnetic transfer characteristics.

Further, US-4,696,869 (JP-95015748 (B)) describes a
10 magnetic recording medium, using ester or trimethylolpropane or ester of pentaerythritol and monoester as lubricants. However, the magnetic layer has low storage property and low resistance to damage. Further, this product has low durability and poor electromagnetic
15 transfer characteristics in high-density recording.

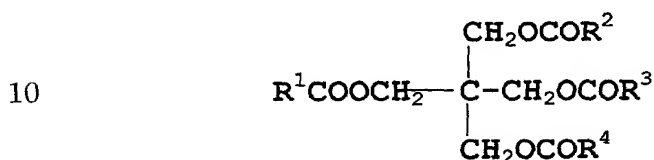
Also, US-5,258,223 (JP-2552958) proposes a magnetic recording medium, which can have higher electromagnetic transfer characteristics in short wavelength recording and which comprises a primer layer and a thin upper magnetic
20 layer. In the prescription as disclosed, the product is not good enough in terms of durability. The storage property of the magnetic layer is low, and resistance to damage of the magnetic layer is not sufficient. Further, the product has low electromagnetic transfer
25 characteristics in high-density recording.

SUMMARY OF THE INVENTION

The present invention provides a magnetic recording

medium, which comprises a primer layer containing at least nonmagnetic powder on a support member and at least one layer of magnetic layer containing ferromagnetic powder dispersed in a binder, the magnetic layer being placed on the support member, wherein the primer layer comprises at least one type of compound expressed by the following general formula (1);

General formula (1)



where R^1 , R^2 , R^3 , and R^4 each represents an alkyl group having 2 to 7 carbon atoms.

Also, the present invention provides the magnetic recording medium as described above, wherein thickness of the magnetic layer is within the range of 0.05 to 1 μm .

Further, the present invention provides the magnetic recording medium as described above, wherein said medium is a disk-type magnetic recording medium.

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DESCRIPTION OF THE PREFERRED EMBODIMENT

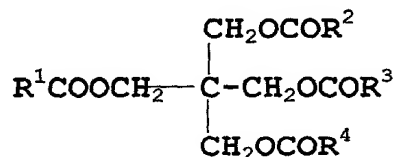
The present invention provides a high-density magnetic recording medium, comprising a lubricant of specific chemical structure for the purpose of achieving high durability and high resistance to damage and wear and good electromagnetic transfer characteristics.

In particular, it has been found in the present invention that, when a tetraester compound is added at

least to a primer layer, and a magnetic layer is coated on the primer layer and dried, and processed by calender processing, very smooth magnetic layer can be obtained. Thus, a magnetic recording medium having high durability
 5 under high temperature and high speed operation can be obtained.

As the lubricant to be used in the present invention, it is preferable to use a tetraester compound expressed by the following general formula:

10 General formula (1):



where R¹, R², R³, and R⁴ each represents an alkyl group
 15 having 2 to 7 carbon atoms, or more preferably having 3 to 5 carbon atoms. If the number of carbon atoms is less than the above value, the product is too volatile. When it is turned to high temperature during friction, surface of the magnetic layer is worn out, and durability is decreased.

20 Hydrophilic property is increased, and durability is decreased under high temperature and high humidity environment. If the number of carbon atoms is more than the above value, viscosity increases. Fluid lubricating performance is decreased, and this leads to lower
 25 durability. For good preservation and stability, it is preferable that saturated hydrocarbon group is contained.

The hydrocarbon group may be either branched or direct chain, while the direct-chain group is more preferable

because viscosity is low and durability is high. Also, R¹, R², R³, and R⁴ are preferably the same but they may be different from each other.

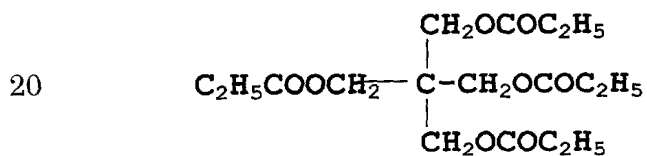
These compounds can be synthesized by a general method
5 for synthesizing fatty acid ester, i.e. synthesizing through reaction of pentaerythritol with fatty acid or fatty acid chloride.

The tetraester compound of the present invention must be contained in the primer layer. Adding quantity of
10 tetraester compound is preferably 0.1 to 50 weight parts, or more preferably 1 to 25 weight parts to 100 weight parts of nonmagnetic powder.

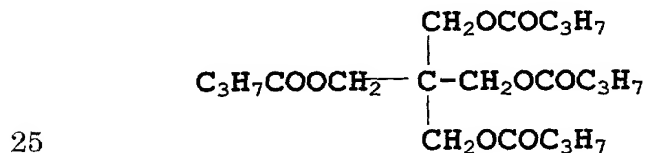
As the tetraester compound expressed by the general formula (1), the following compounds may be used:

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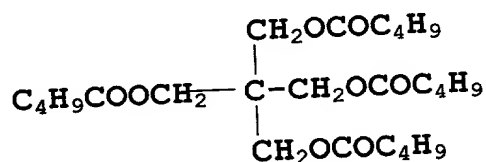
Compound 1



Compound 2

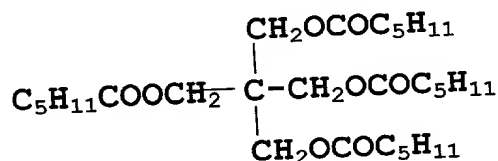


Compound 3



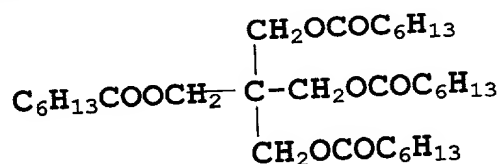
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Compound 4



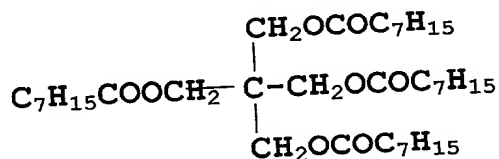
Compound 5

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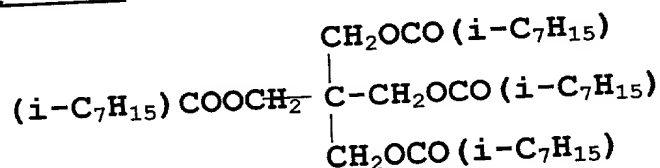
Compound 6

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Compound 7

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In the magnetic recording medium of the present invention, in addition to the lubricant comprising tetraester as expressed by the general formula (1), an additive having lubricating effect, anti-static effect, dispersing effect, plasticizing effect, etc. may be used. For example, molybdenum disulfide, tungsten disulfide, graphite, boron nitride, graphite fluoride, silicone oil, silicone having polar group, fatty acid denatured silicone,

fluorine-containing silicone, fluorine-containing alcohol, fluorine-containing ester, polyolefin, polyglycol, alkyl phosphoric acid ester and its alkali metal salt, alkyl sulfuric acid ester and its alkali metal salt,

5 polyphenylether, phenylphosphonic acid, aminoquinones, various types of silane coupling agents, titanium coupling agents, fluorine-containing alkyl sulfuric acid ester and its alkali metal salt, monobasic fatty acid having 10 to 24 carbon atoms (may contain unsaturated bonding or may be

10 branched) and metal salt (such as Li, Na, K, Cu, etc.), or monohydric, dihydric, trihydric, tetrahydric, pentahydric, or hexahydric alcohol having 12 to 22 carbon atoms (may contain unsaturated bonding or may be branched), alkoxy alcohol having 12 to 22 carbon atoms, mono-fatty acid ester

15 or di-fatty acid ester comprising either one of monobasic fatty acid having 10 to 24 carbon atoms (may contain unsaturated bonding or may be branched) or monohydric, dihydric, trihydric, tetrahydric, pentahydric or hexahydric alcohol (may contain unsaturated bonding or may be

20 branched), or fatty acid ester of monoalkylether of alkylene oxide polymerized product, fatty acid amide having 8 to 22 carbon atoms, aliphatic amine having 8 to 22 carbon atoms, etc. may be used.

As the monoester compound, it is preferable to use

25 saturated fatty acid monoester, unsaturated fatty acid monoester, ester of alkylene oxide added alcohol and fatty acid, etc.

Also, it is preferable to use n-butyl stearate, sec-

butyl stearate, n-butyl palmitate, n-butyl myristate,
isoamyl stearate, isoamyl palmitate, isoamyl myristate, 2-
ethylhexyl stearate, 2-ethylhexyl palmitate, 2-ethylhexyl
myristate, oleyl oleate, oleyl stearate, stearyl stearate,
5 butoxyethyl stearate, butoxydiethylene glycol stearate, etc.

As the fatty acid, it is preferable to use palmitoleic
acid, oleic acid, erucic acid, linoleic acid, stearic acid,
palmitic acid, myristic acid, etc.

As the binder suitable for the magnetic layer and the
10 primer layer, thermoplastic resin, thermosetting resin,
reactive resin or mixture of these compounds may be used.
As the thermoplastic resin, it is preferable to use the
resin, which has glass transition temperature of -100°C to
 $+150^{\circ}\text{C}$, number average molecular weight of 1,000 to 200,000,
15 or more preferably 10,000 to 100,000, and degree of
polymerization of about 50 to 1,000 may be used.

As these compounds, polymer or copolymer containing
the following substance as constituent units or
polyurethane resin, or various types of rubber type resin
20 may be used: vinyl chloride, vinyl acetate, vinyl alcohol,
maleic acid, acrylic acid, acrylic acid ester, vinylidene
chloride, acrylonitrile, methacrylic acid, methacrylic acid
ester, styrene, butadiene, ethylene, vinylbutyral,
vinylacetal, vinylester, etc. As the thermosetting resin
25 or reactive resin, phenol resin, epoxy resin, polyurethane
curing resin, urea resin, melamine resin, alkyd resin,
acryl type reactive resin, formaldehyde resin, silicone
resin, epoxy-polyamide resin, mixture of polyester resin

and isocyanate prepolymer, mixture of polyester polyol and polyisocyanate, mixture of polyurethane and polyisocyanate, etc. may be used. For further details on these resin compounds, reference should be made to: "Handbook of
5 Plastics" published by Asakura Shoten Co., Ltd. Electron beam curing resin already known in the art may be used in each of the above layers. The examples and the manufacturing method are described in detail in JP-A-62-256219. The above resin compounds may be used alone or in
10 combination. As the preferable combinations, a combination of polyurethane resin with at least one type selected from vinyl chloride resin, vinyl chloride - vinyl acetate copolymer, vinyl chloride - vinyl acetate - vinyl alcohol copolymer, or vinyl chloride - vinyl acetate - maleic acid
15 anhydride copolymer, or a combination of polyisocyanate with these compounds may be used.

The tetraester compound of the present invention has high affinity to vinyl chloride type binder or polyurethane type binder, and it is preferable to use these compounds as
20 the binder. In particular, as the binder used in the primer layer, it is preferable to use vinyl chloride type binder or polyurethane type binder.

The vinyl chloride type binder may be copolymerized with the following compounds: acrylic or methacrylic
25 monomer such as alkyl acrylate, alkyl methacrylate, etc., allyl ether such as allylalkylether, fatty acid vinyl ester such as vinyl acetate, vinyl propionate, etc., vinyl monomer such as styrene, ethylene, butadiene, etc., and

further, monomer having functional groups such as hydroxyl group, epoxy group, etc. or polar group as to be described later.

As the polyurethane, polyester urethane, polyether urethane, polyetherester urethane, acrylic polyurethane, etc. may be used.

The polyurethane having glass transition temperature (T_g) of -50°C to +200°C is preferably used, or more preferably 20°C to 100°C. If glass transition temperature is too low, durability is decreased. If it is too high, calender moldability is decreased, and this leads to poor smoothness and low electromagnetic transfer characteristics.

In the binder, it is preferable that -COOM, -SO₃M, -SO₄M, -PO(OM)₂, -OPO(OM)₂, amino group, quaternary ammonium base, etc. are introduced as polar groups in an amount of 1×10^{-5} eq/g to 2×10^{-4} eq/g. If the amount of these polar groups is lower than 1×10^{-5} eq/g, dispersion property is decreased. If it is higher than 2×10^{-4} eq/g, dispersion property is also decreased.

It is preferable that OH group is introduced as curing functional group with isocyanate curing agent, or epoxy group, SH group, CN group, -NO₂ group, etc. may be introduced.

It is preferable that the binder including curing agent is contained in the magnetic layer in an amount of 10 to 25 weight parts to 100 weight parts of the ferromagnetic powder. The content of the binder including curing agent in the magnetic layer is preferably 10 to 25 weight parts

to 100 weight parts of the ferromagnetic powder. The content of the binder in the primer layer is preferably 15 to 40 weight parts to 100 weight parts of nonmagnetic powder. It is preferable that more binder is contained in
5 the primer layer.

As the ferromagnetic powder to be used in the magnetic layer of the present invention, it is preferable to use ferromagnetic alloy powder containing α -Fe as main component. The ferromagnetic powder may contain the
10 following elements in addition to the atoms as already designated: Al, Si, S, Sc, Ca, Ti, V, Cr, Cu, Y, Mo, Rh, Pd, Ag, Sn, Sb, Te, Ba, Ta, W, Re, Au, Pb, Bi, La, Ce, Pr, Nd, P, Co, Mn, Zn, Ni, Sr, B, etc.

In particular, it is preferable that at least one of
15 Al, Si, Ca, Y, Ba, La, Nd, Co, Ni or B is contained in addition to α -Fe, or more preferably at least one of Co, Y or Al. The content of Co is preferably 40 to 100 inclusive of α -Fe in atom ratio, or more preferably 15 to 35 inclusive, or most preferably 20 to 35 inclusive. The
20 content of Y is preferably 1.5 to 12 inclusive to 100 of α -Fe in atom ratio, or more preferably 3 to 10 inclusive, or most preferably 4 to 9 inclusive. The content of Al is preferably 5 to 30 inclusive to 100 of α -Fe, or more preferably 5 to 15 inclusive, or most preferably 7 to 12
25 inclusive. The ferromagnetic powder may be processed in advance with dispersing agent, lubricant, surface active agent, anti-static agent, etc. before dispersion. More concretely, the details are described in: JP-69014090(B),

JP-70018372(B), JP-72022062(B), JP-72022513(B), JP-
71028466(B), JP-71038755(B), JP-72004286(B), JP-72012422(B),
JP-72017284(B), JP-72018509(B), JP-7218573(B), JP-
64010307(B), JP-71039639(B), US-3,026,215, US-3,031,341,
5 US-3,100,194, US-3,242,005, US-3,389,014, etc.

A small quantity of hydroxides or oxides may be
contained in the ferromagnetic alloy powder. The
ferromagnetic alloy powder obtained by the manufacturing
methods already known may be used in the present invention,
10 and the following methods may be used: A method to reduce
complex organic acid salt (mainly oxalic acid salt) using
the reducing gas such as hydrogen, a method to obtain Fe or
Fe-Co particles by reducing iron oxide with reducing gas
such as hydrogen, a method to thermally decompose metal
15 carbonyl compound, a method to reduce by adding reducing
agent such as sodium borohydride, hypophosphite or
hydrazine to aqueous solution of ferromagnetic metal, a
method to obtain fine powder by evaporating metal in an
atmosphere of inert gas under low pressure, etc. The
20 ferromagnetic alloy powder thus obtained may be processed
by one of the following methods: a method for gradual
oxidation, i.e. a method to dry after immersing in organic
solvent, a method to immerse in organic solvent and to form
oxide film on the surface by oxygen-containing gas and to
25 dry, or a method to form oxide film on the surface by
adjusting partial pressure of oxygen gas and inert gas
without using organic solvent.

If the ferromagnetic powder in the magnetic layer of

the present invention is expressed by specific surface area according to BET method, it is 45 to 80 m²/g, or more preferably 50 to 70 m²/g. If it is lower than 40 m²/g, noise increases. If it is 80 m²/g or more, good surface property is not obtained and this is not desirable.

Crystallite size of the ferromagnetic powder of the magnetic layer of the present invention is 8 to 35 nm, or more preferably 10 to 25 nm, or most preferably 14 to 20 nm. Longer axis diameter of the ferromagnetic powder is 0.02 to 0.25 μm inclusive, or more preferably 0.05 to 0.15 μm inclusive, or most preferably 0.06 to 0.1 μm inclusive. Acicular ratio of the ferromagnetic powder is preferably 3 to 15 inclusive, or more preferably 5 to 12 inclusive. The value of σ_s of the magnetic metal powder is preferably 100 to 180 Am²/kg (emu/g), or more preferably 110 Am²/kg (emu/g), or most preferably 125 to 160 Am²/kg (emu/g). Coercive force of metal powder is preferably 111 kA/m to 279 kA/m (1400 Oe to 3500 Oe) inclusive, or more preferably 143 kA/m to 238 kA/m (1800 Oe to 3000 Oe) inclusive.

It is preferable that moisture content of the ferromagnetic powder is in the range of 0.01% to 2%. It is preferable to optimize the moisture content of the ferromagnetic powder depending on the type of the binder.

It is preferable to adjust pH value of the ferromagnetic powder by adjusting combination with the binder used. The preferable pH range is 4 to 12, or it is more preferably 6 to 10. The ferromagnetic powder may be processed by surface treatment using Al, Si, P or oxide of

these elements. The amount of the processed part is preferably 0.1 to 10% of total ferromagnetic powder. When it is processed by surface treatment, adsorption of lubricant by fatty acid or the like is reduced to 100 mg/m² or lower, and this is desirable. The ferromagnetic powder may contain soluble inorganic ions such as Na, Ca, Fe, Ni, Sr, etc. It is preferable that these are not present, but even when these are present in concentration of less than 200 ppm, the properties of the product are not particularly affected. It is preferable that the ferromagnetic powder used in the present invention has less voids. The percentage of the voids contained is preferably 20 vol % or less, or more preferably 5 vol % or less.

The shape of the ferromagnetic powder may be any of needle-like, grain-like or spindle-like shape so far as it satisfies the properties for the particle size. Inverted magnetic field distribution (SFD) of the ferromagnetic powder itself is preferably lower, i.e. 0.8 or lower. The distribution of the value of Hc of the ferromagnetic powder must be lower. If SFD is 0.8 or lower, the product has good electromagnetic transfer characteristics and higher output. Magnetization inversion is sharp, and peak shift occurs less frequently, and the product is suitable for high-density digital magnetic recording. To decrease distribution of Hc, there are methods such as a method to increase particle size distribution of goethite in the ferromagnetic powder or a method to prevent sintering.

As the ferromagnetic powder used in the magnetic layer

of the present invention, hexagonal crystal ferrite powder may be used.

As the hexagonal crystal ferrite, substituent of barium ferrite, strontium ferrite, lead ferrite, calcium ferrite, or Co substituent may be used. More concretely, magnetoplumbite type barium ferrite and strontium ferrite, magnetoplumbite type ferrite with particle surface covered with spinel, or magnetoplumbite type barium ferrite and strontium ferrite partially containing spinel phase may be used. It may contain, in addition to the designated atoms, the following atoms: Al, Si, S, Sc, Ti, V, Cr, Cu, Y, Mo, Rh, Pd, Ag, Sn, Sb, Te, Ba, Ta, W, Re, Au, Pb, Bi, La, Ce, Pr, Nd, P, Co, Mn, Zn, Ni, Sr, B, Ge, Nb, etc. In general, substances added with element such as Co-Ti, Co-Ti-Zr, Co-Ti-Zn, Ni-Ti-Zn, Nb-Zn-Co, Sb-Zn-Co, Nb-Zn, etc. may be used.

In general, substances added with the elements such as Co-Zn, Co-Ti, Co-Ti-Zr, Co-Ti-Zn, Ni-Ti-Zn, Nb-Zn-Co, Sb-Zn-Co, Nb-Zn, etc. may be used. These substances containing impurities, which are unavoidably contained due to raw materials and manufacturing methods, may be used.

Particle size is preferably 10 to 200 nm in hexagonal diameter, or more preferably 20 to 100 nm. When reproduction is performed on the magnetic resistance head, it is necessary to decrease noise, and the plate diameter of 40 nm or lower is preferable. If it is lower than 10 nm, stable magnetization cannot be achieved due to thermal fluctuation. If it is 200 nm or more, noise is increased.

None of these cases is suitable for high-density magnetic recording. Planar ratio (plane diameter/plate thickness) is preferably in the range of 1 to 15, or more preferably 2 to 7. If planar ratio is lower, filling ratio in the magnetic layer is increased and this is desirable, but orientation property is not good enough. If it is higher than 15, noise is increased due to stacking between particles. Specific surface area according to BET method of the particle size range is 10 to 200 m²/g. Specific surface area approximately agrees with the value arithmetically calculated from particle plate diameter and plate thickness. Crystallite size is preferably 5 to 45 nm, or more preferably 10 to 35 nm. Normally, the narrower the distribution of particle plate diameter and plate thickness is, the more it is desirable. Quantification in numerical value is difficult to perform, but comparison can be made by measuring 500 particles at random on the photograph taken under transmission electronic microscope (TEM). Distribution is usually not normal distribution. If it is calculated and expressed in standard deviation to mean size, it is: $\sigma/\text{mean size} = 0.1$ to 2.0. To make the particle size distribution sharper, reaction system to generate particles is turned to more homogeneous, and distribution improving processing is carried out on the generated particles. For instance, a method is known, in which ultra-fine particles are selectively dissolved in acid solution.

Coercive force (Hc) of the magnetic material can be

produced to 39.8 to 398 kA/m (500 Oe to 5000 Oe). The higher the value of H_c is, the more advantageous it is for high-density recording, but there is limitation due to the ability of the recording head. Normally, it is up to about
5 63 to 318 kA/m (800 Oe to 4000 Oe), or more preferably 119 kA/m to 279 kA/m (1500 Oe to 3500 Oe). In case saturation magnetization of the head exceeds 1.4 Tesla, it is preferable to set the value of H_c to 159 kA/m (2000 Oe) or more. The value of H_c can be controlled by particle size
10 (plate diameter and plate thickness), type and quantity of the elements contained, substitution site of element, and reactive condition to generate particles. Saturation magnetization (σ_s) is in the range of 40 to 80 Am²/kg. The higher the value of σ_s is, the more it is desirable. The
15 finer the particles are, the more the value of σ_s decreases. Various methods are known to improve the value of σ_s , i.e. a method to combine spinel ferrite with magnetoplumbite ferrite, or a method to select type and adding quantity of the elements. Also, W type hexagonal
20 crystal ferrite may be used. When the magnetic material is dispersed, the surface of the magnetic particles may be processed using a dispersion agent or a material suitable for polymer. As surface processing material, inorganic compound or organic compound is used. Typical compounds
25 used are: oxide or hydroxide of Si, Al, P, etc., various types of silane coupling agents, or various types of titanium coupling agents. The adding quantity is 0.1 to 10 weight parts to 100 weight parts of the magnetic material.

For the dispersion, pH value of the magnetic material is important. It is normally about 4 to 12, and optimal value is determined according to the dispersion agent and polymer. For chemical stability and preservation property of the medium, pH value of about 6 to 10 is generally chosen. Moisture content in the magnetic material also exerts influence on dispersion. There is the optimal value depending on the dispersion agent and polymer. Normally, the values of 0.01 to 2.0 weight % is selected. Therefore, the following methods are used to produce hexagonal crystal ferrite: (1) Metal oxide to substitute barium oxide, iron oxide and iron are mixed with boron oxide to use as glass generating substance to obtain ferrite composition as desired. Then, the mixture is melted and rapidly cooled to turn to amorphous substance. Then, it is heated again and is then washed and pulverized to barium ferrite crystal powder. This is called glass crystallization method. (2) Solution of barium ferrite composition metal salt is neutralized with alkali. After removing side products, it is heated in liquid phase at 100°C or more. Then, it is washed, dried and pulverized, and barium ferrite crystal powder is obtained. This is called hydrothermal reaction method. (3) Solution of barium ferrite composition metal salt is neutralized with alkali. After removing side products, it is dried and processed at temperature of lower than 1100°C. Then, it is pulverized and barium ferrite crystal powder is obtained. This is called coprecipitation method. Any of the above methods may be used.

Next, description will be given on the primer layer of the magnetic recording medium of the present invention.

Inorganic powder used in the primer layer of the present invention is nonmagnetic powder. For example,

5 inorganic powder can be selected from inorganic compound such as metal oxide, metal carbonate, metal sulfate, metal nitride, metal carbide, metal sulfide, etc. As the inorganic compounds, the following substances are used in combination or alone: For example, α -alumina with alpha
10 ratio of 90% or more, β -alumina, γ -alumina, θ -alumina, silicon carbide, chromium oxide, cerium oxide, α -iron oxide, goethite, corundum, silicon nitride, titanium carbide, titanium oxide, silicon dioxide, tin oxide, magnesium oxide, tungsten oxide, zirconium oxide, boron
15 nitride, zinc oxide, calcium carbonate, calcium sulfate, barium sulfate, molybdenum disulfide, etc. In particular, it is preferable to use titanium dioxide, zinc oxide, iron oxide or barium sulfate, or more preferably titanium dioxide or α -iron oxide because particle size distribution
20 is lower and there are many means for providing the functions. Particle size of the non-magnetic powder is preferably in the range of 0.005 to 2 μm . When necessary, non-magnetic powder with different particle sizes may be mixed together or similar effect can be provided with
25 single type of non-magnetic powder by widening the particle size distribution. In particular, it is preferable that average particle size of the non-magnetic powder is 0.01 to 0.2 μm . In case nonmagnetic powder is particulate metal

oxide, average particle size is preferably 0.8 μm or lower. In case it is needle-like metal oxide, it has preferably longer axis diameter of 0.3 μm or less. Tap density is 0.05 to 2 g/ml, or more preferably 0.2 to 1.5 g/ml.

- 5 Moisture content of the nonmagnetic powder is preferably 0.1 to 5 weight %, or more preferably 0.2 to 3 weight %, or most preferably 0.3 to 1.5 weight %.

Also, pH value of the nonmagnetic powder is preferably in the range of 2 to 11, or more preferably 5.5 to 10.

- 10 Specific surface area of the nonmagnetic powder is preferably in the range of 1 to 100 m^2/g , or more preferably 5 to 80 m^2/g , or most preferably 10 to 70 m^2/g . Crystallite size of the nonmagnetic powder is preferably in the range of 0.004 to 1 μm , or more preferably 0.04 to 0.1
- 15 μm . Oil absorption using DBP (dibutyl phthalate) is preferably in the range of 5 to 100 ml/100 g, or more preferably 10 to 80 ml/100 g, or most preferably 20 to 60 ml/100 g. Specific gravity is preferably in the range of 1 to 12, or more preferably 3 to 6. The shape of the
- 20 nonmagnetic powder may be any of needle-like, spherical, polygonal, or planar shape.

- Ignition loss is preferably 20 weight % or less. Most preferably, there is no ignition loss. Morse hardness of the nonmagnetic powder used in the present invention is
- 25 preferably 4 or more and 10 or less. Roughness factor of the surface of the powder is preferably in the range of 0.8 to 1.5, or more preferably 0.9 to 1.2. Stearic acid adsorption of the nonmagnetic powder is preferably in the

range of 1 to 20 $\mu\text{mol}/\text{m}^2$, or more preferably 2 to 15 $\mu\text{mol}/\text{m}^2$, or most preferably 3 to 8 $\mu\text{mol}/\text{m}^2$.

Heat of wetting of the nonmagnetic powder to water at 25°C is preferably in the range of 0.2 to 0.6 J/m². Also, a solvent with heat of wetting in the above range can be used.

It is preferable that pH value is in the range of 3 to 6. The nonmagnetic powder preferably contains water-soluble sodium in the range of 0 to 150 ppm, and water-soluble calcium in the range of 0 to 50 ppm.

It is preferable that surface of the non-magnetic powder is processed by surface treatment using Al₂O₃, SiO₂, TiO₂, ZrO₂, SnO₂, Sb₂O₃, ZnO₂ or Y₂O₃. To ensure better dispersion property, it is preferable to use Al₂O₃, SiO₂ or ZrO₂. These substances may be used in combination or alone. According to each individual purpose, coprecipitated surface treatment layer may be used, or a method to treat the surface layer using silica after treating with alumina, or a method reversing this procedure may be adopted. The surface treatment layer may be porous according to the purpose. In general, it is preferably homogeneous and dense.

Concrete examples of the nonmagnetic powder used in the primer layer of the present invention are: Nanotite (manufactured by Showa Denko Co., Ltd.), HIT-100 and ZA-G1 (manufactured by Sumitomo Chemical Industry Co., Ltd.), α -hematite DPN-250, DPN-250BX, DPN-245, DPN-270BX, DBN-SA1, and DBN-SA3 (manufactured by Toda Industry Co., Ltd.), titanium oxide TTO-51B, TTO-55A, TTO-55B, TTO-55C, TTO-55S,

TTO-55D, SN-100, α -hematite E270, E271, E300, and E303 (manufactured by Ishihara Industry Co., Ltd.), titanium oxide STT-4D, STT-30D, STT-30, STT-65C, and α -hematite α -40 (manufactured by Titanium Industry Co., Ltd.), MT-100S, 5 MT-100T, MT-150W, MT-500B, MT-600B, MT-100F, and MT-500HD (manufactured by Teika Co., Ltd.), FINEX-25, BF-1, BF-10, BF-20, and ST-M (manufactured by Sakai Chemical Industry Co., Ltd.), DEFIC-Y and DEFIC-R (manufactured by Dowa Mining Co., Ltd.), AS2BM and TiO₂ P25 (manufactured by 10 Japan Aerogil), and 100A and 500A and fired products of these materials (manufactured by Ube Industries, Ltd.).

The most preferable nonmagnetic powders are titanium dioxide and α -iron oxide.

When carbon black is mixed in the primer layer, it is 15 possible to decrease surface electrical resistance R_s as already known, and light transmittance can be decreased. Also, micro-Vickers hardness as desired can be obtained. Further, by adding carbon black to the primer layer, it is possible to obtain good effect for storage of lubricant. 20 The types of carbon black used for this purpose are: Furnace black for rubber, thermal black for rubber, black for color, acetylene black, etc. In the carbon black to be added to the primer layer, the following properties should be optimized, and when these are simultaneously used, 25 better effects can be attained.

Specific surface area of the carbon black is preferably 100 to 500 m²/g, or more preferably 150 to 400 m²/g. DBP oil absorption is preferably 20 to 400 ml/100 g,

or more preferably 30 to 200 ml/100 g. Particle size of the carbon black is preferably 5 to 80 μ m, or more preferably 10 to 50 μ m, or most preferably 10 to 40 μ m. In the carbon black, it is preferable that pH value is 2 to 10, moisture content is 0.1 to 10%, and tap density is 0.1 to 1 g/ml. Concrete examples of the carbon black to be used in the present invention are as follows: Blackpearls 2000, 1300, 1000, 900, 800, 880, 700, and Vulcan XC-72 (manufactured by Cabot), #3050B, #3150B, #3250B, #3750B, #3950B, #950, #650B, #970B, #850B, MA-600, MA-230, #4000, and #4010 (manufactured by Mitsubishi Chemical Industry Co., Ltd.), Conductex SC, Raven 8800, 8000, 7000, 5750, 5250, 3500, 2100, 2000, 1800, 1500, 1255, and 1250 (manufactured by Columbia Carbon Co.), and Ketchenblack EC (manufactured by Ketchenblack International). Carbon black may be processed by surface treatment using dispersion agent, or it may be graphitized with resin and used, or a part of the surface may be graphitized and used. Carbon black may be dispersed with the binder in advance before it is added to the coating material. These types of carbon black can be used within the range not exceeding 50 weight % to the inorganic powder and within the range not exceeding 40% of total weight of the primer layer. These types of carbon black may be used alone or in combination. For further details of the carbon black to be used in the present invention, reference should be made to: "Handbook of Carbon Black" (compiled by Carbon Black Association of Japan).

Also, organic powder may be added to the primer layer. For example, acrylstyrene type resin powder, benzoguanamine resin powder, melamine resin powder, or phthalocyanine type pigment may be used. Also, polyolefin type resin powder, polyester type resin powder, polyamide type resin powder, polyimide type resin powder, or polyfluoride ethylene resin may be used. The methods for manufacturing these types of resin powder are described in JP-62018564(A) and JP-600255827(A).

As the binder resin, lubricant, dispersion agent, additive, solvent, dispersing procedure, etc. of the primer layer, those for the magnetic layer as described below can be applied. In particular, for the quantity and type of resin in the binder, adding quantity and type of the additive and dispersion agent, the technique already known for the magnetic layer can be applied.

A coating solution prepared from the above materials is coated on a nonmagnetic support member, and a primer layer or a magnetic layer is formed. As the nonmagnetic support member to be used in the present invention, polyethylene naphthalate, polyethylene terephthalate, polyamide, polyimide, polyamideimide, aromatic polyamide, polybenzoxidazole, etc. processed by biaxial stretching may be used. More preferably, polyethylene naphthalate and aromatic polyamide may be used. These nonmagnetic support member may be processed in advance by corona discharge, plasma treatment, process to make more easily adhesive, heat treatment. Also, the nonmagnetic support member used

in the present invention preferably has surface with good smoothness, i.e. average surface roughness on the central line in the range of 0.1 to 20 nm, or more preferably 1 to 10 nm with cutoff value of 0.25 mm. Also, it is preferable
5 that these nonmagnetic support members have not only lower average surface roughness on the central line but also have no coarse projection of higher than 1 μ m.

The thickness of the nonmagnetic support member of the magnetic recording medium of the present invention is
10 preferably in the range of 4 to 100 μ m.

On the surface not coated with the magnetic coating material of the nonmagnetic support member of the present invention, a back-coating layer (backing layer) may be provided. The back-coat layer is a layer coated on the
15 surface of the nonmagnetic support member where the magnetic coating material is not coated and where a coating material for forming the back-coat layer is coated. The coating material for forming the back-coat layer is obtained by dispersing granular components such as
20 abrasives, anti-static agents, etc. and a binder in organic solvent. As the granular components, various types of inorganic pigments or carbon black may be used. As the binder, nitrocellulose, phenoxy resin, vinyl chloride type resin, or polyurethane may be used alone or as a mixture of
25 these components. An adhesive layer may be provided on the surface where the magnetic coating material and the coating material for forming the back-coat layer is coated on the nonmagnetic support member of the present invention.

To produce the magnetic recording medium of the present invention, a coating solution for the primer layer and a magnetic coating solution are coated to a given thickness on the surface of the nonmagnetic support member under running condition. The coating solution for the primer layer and the coating solution for the magnetic layer may be coated sequentially or in multiple layers at the same time.

As the coating device to coat the coating solution for the primer layer or the magnetic coating solution, the following devices may be used: air doctor coat, blade coat, rod coat, extrusion coat, air knife coat, squeeze coat, impregnation coat, reverse roll coat, transfer roll coat, gravure coat, kiss coat, cast coat, spray coat, spin coat, etc.

For further details, reference should be made, for example, to "The Newest Coating Technique" published by Sogo Gijutsu Center, Ltd. (May 31, 1983). In case the present invention is applied to a magnetic recording medium comprising two layers or more, the following can be recommended as examples of the coating device and method:

- (1) Using a coating device such as gravure, roll, blade, extrusion, etc. generally applied in the coating of the coating material, the primer layer is coated at first.
- While the primer layer is not yet dried, the upper layer is coated using a support pressurizing type extrusion coating device as disclosed, for example, in JP-B-88046186, JP-A-60-238179, JP-A-2-265672, etc.

(2) Using a coating head having two slits for allowing the coating solution to pass as disclosed in JP-A-63-88080, JP-A-2-17971 or JP-A-2-265762, the upper and the lower layers are coated almost at the same time.

- 5 (3) Using an extrusion coating device equipped with backup roll as disclosed in JP-A-2-174965, the upper and the lower layers are coated almost at the same time. The coating layer of the coating solution for the magnetic layer is dried after magnetic field orientation processing is performed on the ferromagnetic powder contained in the coating layer of the coating solution for the magnetic layer.
- 10

After it has been dried as described above, surface smoothening treatment is carried out on the coating layer.

- 15 For the surface smoothening treatment, super calender roll is used, for example. By the surface smoothening treatment, the voids generated due to removal of the solvent during drying are eliminated, and filling ratio of the ferromagnetic powder in the magnetic layer is improved.
- 20 This makes it possible to obtain a magnetic recording medium having high electromagnetic transfer characteristics. As the calender processing roll, heat-resistant plastic roll made of epoxy resin, polyimide, polyamide, polyamideimide, etc. is used. Or, a metal roll may be used.

- 25 To perform the processing, the magnetic layer formed by selecting a specific type of ferromagnetic powder and binder as described above is processed by the above calender processing. The conditions for the calender

processing are as follows: The temperature of calender roll is preferably in the range of 60°C to 100°C, or more preferably 70°C to 100°C, or most preferably 80°C to 100°C. The pressure is preferably within the range of 98.0 to 490 kN/m, or more preferably 196 to 441 kN/m, or most preferably 294 to 392 kN/m. The magnetic recording medium thus obtained can be cut to the size as desired using a cutter.

The thickness of the magnetic layer of the magnetic recording medium of the present invention is preferably in the range of 0.05 to 1 μm .

Because the thickness of the magnetic layer is set to as thin as 0.05 to 1 μm in the magnetic recording medium of the present invention, a magnetic recording medium having high electromagnetic transfer characteristics can be obtained.

In the magnetic recording medium of the present invention, it is possible to obtain a surface with high smoothness, i.e. average roughness on the central line of the surface is preferably in the range of 1.0 to 3.5 nm or more preferably 1.0 to 3.0 nm with cutoff value of 0.25 μm .

As described above, the magnetic recording medium of the present invention is characterized in that a magnetic layer with very smooth surface can be formed, and it has high durability - in particular, high durability under high temperature and high speed conditions.

In particular, the combination with the primer layer is important for the improvement of the surface smoothness,

and such smoothness cannot be expected in the conventional type magnetic recording medium with single magnetic layer.

Even when the tetraester compound is added only to the primer layer, it comes out gradually to the surface of the magnetic layer after the magnetic recording medium has been produced, and the effects to improve the durability are high.

With the arrangement as described above, high durability is compatible with good electromagnetic transfer characteristics in the magnetic recording medium of the present invention compared with the conventional products. It has been found that a tape for video system with high recording density such as DVC or DVC-PRO can be produced in the tape-type medium. In disk-type medium, superb durability can be achieved in a recording system such as Zip with high speed operation of 700 rpm or more.

The magnetic recording medium as described above has very smooth surface to attain high electromagnetic transfer characteristics. When the recording head runs and slides on such smooth surface, it is very difficult to maintain high durability in the conventional technique. For example, in the monoester lubricant known in the past and described in the embodiment of Japanese Patent 2552958 as given above, it is difficult to maintain sufficient durability.

Further, to obtain the magnetic recording medium having high electromagnetic transfer characteristics of the present invention, it is important to have the thickness of the magnetic layer within the range of 0.05 to 1 μ m. In

case a thin magnetic layer is provided directly on the support member, the durability is not high enough even when tetraester with high lubricant property is added.

The smoothness of the magnetic layer is also insufficient and noise increases, and it is not possible to have high electromagnetic transfer characteristics. However, it has been found that, when tetraester compound of the present invention is added at least to the primer layer, very smooth magnetic layer can be formed if a magnetic layer is coated on it and dried and it is further processed by calender.

The tetraester compound of the present invention is characterized in that it is easily mixed with binder. As a result, even when molecules become larger, the decrease of liquid lubricant property due to the increase of viscosity does not occur, and smoothness is improved when it is processed by calender.

Further, it has been found that the product has very high durability - in particular, under high temperature and high speed conditions. The combination with the primer layer is important for the improvement of smoothness, and the effects can be attained, which are not expectable in the conventional type magnetic recording medium with single magnetic layer. Even when the tetraester compound is added only to the primer layer, it gradually comes out to the surface of the magnetic layer after the magnetic recording medium is produced, and high durability can be obtained.

(Embodiments)

In the following, description will be given on examples of the present invention to explain the features of the invention. In the examples, the term "part(s)" means "weight part(s)".

5 (Examples 1 to 7 and Comparative example 3)

(Preparation of magnetic solution for the upper layer)

Ferromagnetic alloy powder A 100 parts

Composition: Fe:Co:Al:Y = 100:20:9:6 (atom ratio)

Hc: 159 kA/m (2000 Oe)

10 Crystallite size: 15 nm

BET specific surface area: 59 m²/g

Longer axis diameter: 0.09 μm

Acicular ratio: 7

σ_s: 140 Am²/kg

15 The above powder was pulverized for 10 minutes using an open kneader. Next, the following substances were added:

Vinyl chloride type copolymer

(MR110; Nippon Zeon Co., Ltd.) 7.5 parts

Sulfonic acid-containing polyurethane resin

20 (UR8200; Toyobo, Co., Ltd.) (solid matter)

5 parts

Cyclohexanone

60 parts

The mixture was kneaded for 60 minutes. Then, the following substances were added:

25 α-alumina (HIT55; Sumitomo Chemical Industry Co., Ltd.) 10 parts

Carbon black (#50; Asahi Carbon Co., Ltd.) 3 parts

Methyl ethyl ketone/toluene (1:1 in weight ratio)

200 parts

The mixture was dispersed in a sand mill for 120 minutes.

Then, the following substances were added:

5	Polyisocyanate (Coronate 3041; Nippon Urethane Co., Ltd.) (solid matter)	5 parts
	Compound of Table 1	4 parts
	Stearic acid	1 part
	Oleic acid	1 part
	Methyl ethyl ketone	50 parts

10 The mixture was further agitated and mixed for 20 minutes and was filtered using a filter having average bore diameter of 1 μm , and a magnetic coating material was prepared.

(Preparation of nonmagnetic solution for the primer layer)

15	Titanium oxide	85 parts
	Average particle size: 0.035 μm	
	Crystal type: rutile	
	TiO ₂ content: 90% or more	
	Surface treatment layer: alumina	
20	S _{BET} : 35 to 42 m ² /g	
	True specific gravity: 4.1	
	pH: 6.5 to 8.0	

	Carbon black	15 parts
	(Ketchenblack EC; Ketchenblack International)	

25 The mixture was pulverized for 10 minutes using an open kneader. Next, the following substances were added:

	Vinyl chloride type copolymer	
	(MR110; Nippon Zeon Co., Ltd.)	17 parts

Sulfonic acid-containing polyurethane resin

(UR8200; Toyobo Co., Ltd.) (solid matter)

10 parts

Cyclohexanone

60 parts

5 The mixture was kneaded for 60 minutes. Then,

Methyl ethyl ketone/cyclohexanone

(6:4 in weight ratio)

200 parts

were added, and the mixture was dispersed in a sand mill for 120 minutes. Then, the lubricant of Table 1 and the

10 following substances were added:

Polyisocyanate (Coronate 3041; Nippon Polyurethane Co.,

Ltd.) (solid matter)

5 parts

Stearic acid

1 part

Oleic acid

1 part

15 Methyl ethyl ketone

50 parts

The mixture was agitated and mixed for 20 minutes and was filtered through a filter having average bore size of 1 μm , and a nonmagnetic coating material was prepared.

(Preparation of magnetic recording medium)

20 On the surface of a polyethylene terephthalate support

member of 62 μm in thickness, the nonmagnetic coating material prepared above was coated in thickness of 1.5 μm .

Immediately thereafter, the magnetic coating material was coated to have thickness of 0.2 μm after drying by

25 simultaneous multi-layer coating. When the two layers were not yet dried, this was passed through an AC magnetic field generating system under two different conditions of 50 Hz in frequency and 2.5×10^{-2} Tesla and 50 Hz in frequency

and 1.2×10^{-2} Tesla respectively for random orientation processing. Then, after drying, it was processed by 7-stage calendering under the condition of: 100 m/min in speed, 2.94×10^5 N/m (300 kg/cm) in linear pressure, and 5 90°C in temperature. The product was punched to prepare 3.7-type disk-type medium. After surface polishing treatment, it was mounted on a cartridge for ZIP (Iomega Inc.) with a liner provided on inner side, and a magnetic recording medium comprising floppy disk was prepared. The 10 product was evaluated by the evaluation methods given below. (Comparative examples 1 and 2)

A floppy disk was prepared by the same procedure as in Example 1 except that the primer layer was not coated, and the magnetic layer was coated directly on the support 15 member.

(Evaluation methods)

1. Electromagnetic transfer characteristics

The test was performed using a disk evaluation system (RWA1001; manufactured by Guzik Inc., U.S.A.) and a spin 20 stand (LS-90; manufactured by Kyodo Electronic System). A metal in-gap head with gap length of $0.3 \mu\text{m}$ was used, and reproduction output (TAA) at linear recording density of 60 kfc/i at a position of 24.6 mm in radius was determined. Noise level after DC demagnetization was measured, and S/N 25 value was obtained. Regarding S/N of Comparative example 1 was regarded as 0 dB, evaluation was made on relative S/N value.

2. Durability

Using a floppy disk drive (ZIP100; Iomega Inc.; number of revolutions 2968 rpm), the head was fixed at a position of 38 mm in radius, and recording was performed at recording density of 34 kfc. Then, the signal was reproduced, and this was regarded as 100%. Then, the product was put in running operation for 1500 hours in the following two environmental conditions: 55°C and 20% relative humidity, and 25°C and 50% relative humidity.

For every 24 hours of running operation, the output was monitored. When it was 70% or less of the initial value, it was defined that the service life has expired, and the time was recorded.

3. Calender moldability

After processing by calender, surface roughness of the magnetic layer was measured. Using digital optical profimeter (manufactured by WYKO), average roughness Ra on the central line was measured with cutoff value of 0.25 mm by optical interference method, and the decrease of surface roughness by calendering was determined.

Table 1

	Compound structure	R ¹	R ² , R ³ , R ⁴
Compound 1	General formula (1)	-C ₂ H ₅	-C ₂ H ₅
Compound 2	General formula (1)	-C ₃ H ₇	-C ₃ H ₇
Compound 3	General formula (1)	-C ₄ H ₉	-C ₄ H ₉
Compound 4	General formula (1)	-C ₅ H ₁₁	-C ₅ H ₁₁
Compound 5	General formula (1)	-C ₆ H ₁₃	-C ₆ H ₁₃
Compound 6	General formula (1)	-C ₇ H ₁₅	-C ₇ H ₁₅
Compound 7	General formula (1)	-(i-C ₇ H ₁₅)	-(i-C ₇ H ₁₅)
Compound 8	n-butyl stearate		

Table 2

	Compound		Electro-magnetic transfer characteristics S/N (dB)	Durability (hour)		Calender moldability		
	Upper magnetic layer	Primer layer		25°C	55°C	After coating Ra (nm)	After calendering	
				50%RH	50%RH		Ra (nm)	ΔRa (nm)
Example 1	Compound 1	Compound 1	1.5	1300	1100	11.5	2.7	8.8
Example 2	Compound 2	Compound 2	1.6	1500	1300	11.8	2.7	9.1
Example 3	Compound 3	Compound 3	1.6	1500	1500	11.7	2.6	9.1
Example 4	Compound 4	Compound 4	1.6	1500	1500	11.5	2.6	8.9
Example 5	Compound 5	Compound 5	1.6	1500	1500	11.8	2.8	9.0
Example 6	Compound 7	Compound 7	1.4	1400	1500	11.6	3.1	8.5
Example 7	Not added	Compound 3	1.5	1500	1500	11.9	2.8	9.1
Comparative example 1	Compound 8	-	0	123	31	12.3	4.2	8.1
Comparative example 2	Compound 3	-	0.1	185	50	12.1	3.9	8.2
Comparative example 3	Compound 8	Compound 8	0	142	41	12.4	4.3	8.1

As described above, using a magnetic recording medium with tetraester having a specific chemical structure added at least in the primer layer, it is possible to improve electromagnetic transfer characteristics. Durability was improved in a disk-type magnetic recording medium of high recording density. In particular, the durability under high temperature condition was improved, and a magnetic layer with high calender moldability and smooth surface was produced.